

**Potential-Dependent Electrode-Adsorbate Bonding:
New Insights from Vibrational Spectroscopy
combined with Density Functional Theory**

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Recent years have witnessed important advances in the application of *in-situ* vibrational spectroscopy for elucidating adsorbate structure, bonding, and reactivity at electrochemical interfaces. Most commonly, infrared reflection-absorption spectroscopy (IRAS) has been utilized. While valuable, especially for single-crystal characterization, IRAS suffers from sensitivity and wavenumber-range limitations. The other major vibrational method, surface-enhanced Raman spectroscopy (SERS), has been used chiefly to characterize coinage-metal substrates. However, by utilizing overlayer-deposition strategies with gold substrates, SERS can be harnessed to acquire rich vibrational spectra on a broad range of electrode materials, including transition metals and other catalytically important surfaces (1). A crucial attribute of SERS is the ability to detect vibrational modes over wide frequency ranges, including the low-wavenumber region associated with metal-adsorbate modes. Nonetheless, while vibrational spectroscopy can yield detailed insight into potential-dependent adsorbate structure, fundamental understanding of surface-chemical bonding requires additional information which is usually not experimentally accessible in electrochemical systems.

However, the recent emergence of Density Functional Theory (DFT) for describing adsorbate energetics at metal surfaces offers a valuable means of forging a detailed quantum-chemical picture of potential-dependent bonding interactions. In particular, DFT can be utilized both to aid the structural interpretation of vibrational spectra and to relate them to fundamental bond energy and geometry parameters. Two types of applications of DFT to electrochemistry will be described. The first, which will be emphasized in this talk, involves elucidating the relation between potential-dependent metal-adsorbate bond frequencies (i.e., Stark-tuning behavior) and bonding energetics in terms of metal-adsorbate charge polarization (2-5). A general treatment will be outlined in which the potential-dependent bond energies are described in terms of metal-adsorbate static dipole moments, whereas the potential-dependent bond frequencies reflect primarily the influence of the dynamic dipole moment. The second entails determining band assignments of Raman spectra for complex organic adsorbates, and understanding adsorption-induced frequency shifts in terms of mode-sensitive surface-bonding interactions (6).

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